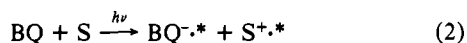


It is also feasible, however, that polarization of the sulfur radical cation derives directly from a primary photochemical charge-transfer reaction:



Indeed, much of our previous effort in CIDEP studies of quinone/organometal systems^{11,12} involves such a primary charge-transfer mechanism. Nevertheless, in the present model sulfur system $\text{BQ}^{\cdot-}$ and the semiquinone radical have not been observed in all the experiments. Furthermore, in a majority of the experiments, both $\text{BQ}^{\cdot+}$ and $\text{S}^{\cdot+}$ radical cations are clearly observable simultaneously, since their *g* factors are substantially different. Both $\text{BQ}^{\cdot+}$ and $\text{S}^{\cdot+}$ exhibit the totally emissive polarization, consistent with the photochemical triplet mechanism and the secondary polarization transfer in (1).

All experiments were performed at room temperature except in cases in which T_1 of the organosulfur cation radicals are too short for CIDEP measurements. Samples were contained in Pyrex tubings and sealed off under high vacuum. ESR observations were made on a Varian E3 X-band spectrometer with 100-kHz field modulation for cw experiments. Time-resolved CIDEP experiments were carried out by using a megawatt nitrogen laser and direct ESR detection, as previously described.¹⁶ The transient polarization was analyzed to obtain T_1 . The detailed analysis reported earlier^{16,17} showed that the ESR signal $h(t)$ at time t from a CIDEP spectrometer with a unique exponential response is

$$h(t) = b_1 + b_2 e^{-\lambda_1 t} + b_3 e^{-\lambda_2 t} + b_4 e^{-t/\tau}$$

where constants b_1 , b_2 , b_3 , and b_4 are related to the initial polarization, the equilibrium polarization, the amplitude B_1 of the microwave magnetic field, the instrument response time τ , and the parameters λ_1 and λ_2 . The λ_1 and λ_2 respectively approach T_1^{-1} and T_2^{-1} as the microwave power approaches zero. In our experiments when T_1 is significantly longer than T_2 and τ , an estimate of T_1 can be reliably obtained by extrapolating measured decay times for a sequence of low microwave powers to zero power.

The organosulfur compounds studied in this report include thianthrene, phenothiazine, thioxanthene-9-one, dibenzothiophene, 4,4'-thiodiphenol, and thianaphthene. With the exception of the last compound, all of these radical cations exhibit totally emissive polarization and their T_1 's are reported in Table I. For thianaphthene, although no transient CIDEP could be detected, it was clear that reaction 1 took place in cw experiments. The lack of observable polarization in this case could be due to the much shorter T_1 for this sulfur radical cation and/or the slower charge-transfer reaction between $\text{BQ}^{\cdot+}$ and thianaphthene. It is worth pointing out that in the same system, the polarization from $\text{BQ}^{\cdot+}$ was indeed observable. T_1 's of the other organosulfur cation radicals are also relatively short, as compared to the "smaller" $\text{BQ}^{\cdot+}$ radical cation in the same system. Our earlier theoretical analyses^{17,18} showed that T_1 is sensitive to both the molecular size and the number of rings in the semiquinone radicals. This may have some bearing on the difference between the "three-ring" and the "two-ring" sulfur compounds. The comparison between the thianthrene and benzoquinone probably will have to take into account the large spin-orbit coupling of the S atom(s), which could contribute to a shorter T_1 .

The ESR and CIDEP results presented here clearly define a useful model reaction using the simple charge-transfer process of a benzoquinone cation radical to organosulfur compounds. The charge-transfer reaction studied here can obviously be applied to other classes of organic donors. In systems where the specific charge-transfer mechanism is complicated by other thermal electron-transfer processes, application of the time-resolved CIDEP

technique should be of great help in delineating the mechanism. Current studies include further exploration of the use of related solvents other than trifluoroacetic acid as well as other organic donors including the sulfoxides.

Acknowledgment. This research is supported by the Natural Sciences and Engineering Research Council of Canada.

Absence of an α -Effect in the Gas-Phase Nucleophilic Reactions of HOO^-

Charles H. DePuy,* Ernest W. Della,¹ Jonathan Filley, Joseph J. Grabowski, and Veronica M. Bierbaum

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received November 15, 1982

In solution nucleophiles that contain a heteroatom adjacent to the reaction center (HOO^- , ClO^- , HONH_2 , etc.) are found to be more reactive toward carbon electrophiles than would be expected from their basicity (the α -effect²). For example, in a recent study HOO^- was shown to undergo $\text{S}_{\text{N}}2$ displacement on a methyl group 10 times faster than does CH_3O^- , despite the greater basicity of the latter anion.³ Even larger effects are found for reactions at unsaturated carbons.⁴ The origin of this phenomenon remains a subject of active discussion. Some explanations invoke special solvation effects such as reduced solvation of the α -nucleophile.⁵ More commonly, it is proposed that electronic repulsions between the lone pair on the heteroatom and those on the nucleophilic center lead to an increase in reactivity for α -nucleophiles,⁶ and a number of workers have advanced quantum mechanical explanations based on this model.⁷ However, these explanations have recently been challenged by Wolfe.⁸ If the α -effect is an intrinsic property of the anion, as these latter explanations suggest, it should manifest itself in the gas phase, while if it is due to differential solvation, it should not. We report that in the gas phase HOO^- shows no evidence of an enhanced nucleophilicity, as compared to HO^- , toward either saturated or unsaturated carbon.

The α -effect is most pronounced for HOO^- , and the most extensive theoretical work has been reported for this anion.^{7c} We have been interested for some time in the chemistry⁹ of HOO^- and recently reported measurements of its basicity and electron binding energy.¹⁰ In order to test its nucleophilicity we first

(1) The Flinders University of South Australia, Bedford Park, South Australia 5042.

(2) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16-24.

(3) Buncel, E.; Wilson, H.; Chuaqui, C. *J. Am. Chem. Soc.* **1982**, *104*, 4896-4900.

(4) For example, HOO^- reacts 10^4 times more rapidly than HO^- with the sp^2 carbon of the malachite green cation (Dixon, J. E.; Bruice, T. C. *J. Am. Chem. Soc.* **1971**, *93*, 6592-6597), and similar large HOO^-/HO^- rate ratios have been observed for reaction at carbonyl (Jencks, W. P.; Carriolo, J. *J. Am. Chem. Soc.* **1960**, *82*, 1778-1786) and cyano (Wiberg, K. B. *J. Am. Chem. Soc.* **1955**, *77*, 2519-2522) groups.

(5) Bunton, C. A. In "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Interscience: New York, 1962; p 25.

(6) Ibne-Rasa, K. M.; Edwards, J. O. *J. Am. Chem. Soc.* **1962**, *84*, 763-768.

(7) (a) Hudson, R. F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 36-56. (b) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976. (c) Heaton, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 2004-2008.

(d) For another explanation, see: Hoz, S. *J. Org. Chem.* **1982**, *47*, 3545-3547.

(8) (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694-7696. (b) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B.; Minot, C.; Eisenstein, O. *Tetrahedron Lett.* **1982**, *23*, 615-618.

(9) DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920-2921.

(10) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H.; Mead, R. D.; Schulz, P. A.; Lineberger, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6262-6263.

(16) DeBoer, J. W. M.; Chung, T. Y. C.; Wan, J. K. S. *Can. J. Chem.* **1979**, *57*, 2971.

(17) Hutchinson, D. A.; Depew, M. C.; Russell, K. E.; Wan, J. K. S. *Macromolecules* **1982**, *15*, 602.

(18) Hutchinson, D. A.; DeBoer, J. W. M.; Wan, J. K. S. *Chem. Phys.* **1980**, *53*, 149.

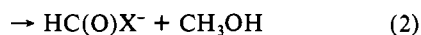
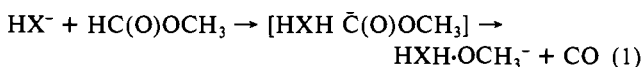
Table I. Reaction Pathways with Methyl Formate^a

	proton abstraction, %	carbonyl addition, %	S _N 2 displacement, %
H ¹⁸ O ⁻	61	34	5
HOO ⁻	64	28	8

^a Both nucleophiles react at the collision rate $k = 2.0 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹ for HO⁻ and 1.9×10^{-9} cm³ molecule⁻¹ s⁻¹ for HOO⁻. The initial product distributions were obtained by extrapolating product percentages to zero neutral flow.

measured the rate of its reaction with methyl fluoride and found it to be somewhat less reactive than either HO⁻ or CH₃O⁻, as would be predicted from its lesser basicity; it therefore displays no detectable α -effect in this S_N2 reaction. However the rate differences are small, and the results could hardly be considered as conclusive, particularly since the energy available for reaction in each case (the ion-dipole binding energy in the reaction complex between the anion and methyl fluoride) will not necessarily be the same for each nucleophile.

A more stringent test would involve a comparison of relative rates among competing reaction channels within a single reaction complex. For this purpose methyl formate is the ideal neutral substrate, for it reacts with bases in three competitive ways, by proton abstraction (eq 1), by B_{AC}2 addition to the carbonyl (eq



2), and by S_N2 displacement on methyl (eq 3).¹¹ The first of these reactions should not be influenced by the α -effect, while the latter two reactions should be. We have therefore compared the branching ratios for the reactions¹² of H¹⁸O⁻ and HOO⁻ with methyl formate in the gas phase by using both a flowing afterglow apparatus and a recently constructed selected ion flow tube (SIFT).¹³ The results are collected in Table I.¹⁴

The rate-determining step in both of these processes is the collision between the ion and the neutral; once the reaction complex is formed, both reactions proceed to completion. However, the relative rates of proton abstraction, nucleophilic addition to the carbonyl group and S_N2 displacement on the methyl group, are the same for the two anions. Thus HOO⁻ shows no enhanced nucleophilic reactivity compared to HO⁻ in the gas phase, and we conclude that the α -effect is most likely a manifestation of solvent effects.

Acknowledgment. We gratefully acknowledge support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. HOO⁻, 14691-59-9; H¹⁸O, 65553-37-9; methyl formate, 107-31-3.

(11) Takashima, K.; Riveros, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 6128-6132.

(12) The isotope tracer was necessary to distinguish the products in eq 2 and 3.

(13) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.*, in press.

(14) The experiments were carried out at room temperature and at 0.3 torr of He. For reactions of HOO⁻ three ions corresponding to the products of eq 1-3 were the only products. Reactions with HO⁻ are more exothermic, and two additional ions, CH₃O⁻ (22%) and M-1 (17%) also appear. CH₃O⁻ could arise either from reaction 1 or 2; following Riveros we assign it to (1). If it arises from (2), our conclusions are strengthened. HO⁻ but not HOO⁻ is strong enough a base to abstract a proton from the ester to form the M-1 ion. Our conclusions are not affected if some or all of the M-1 ion results from proton abstraction from the methyl group (see: Bartmess, J. E.; Caldwell, G.; Rozeboom, M. D. Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI, June 6-11, 1982.

First In-Plane Coordination of a Simple Monoolefin in a Square-Planar Complex. Molecular Structure of η^3 -Methallyl(triphenylphosphine)(styrene)platinum(II) Cation

Kunio Miki,[†] Yasushi Kai,[†] Nobutami Kasai,^{*†} and Hideo Kurosawa^{*†}

Department of Applied Chemistry and
Department of Petroleum Chemistry, Osaka University
Yamadaoka, Suita, Osaka 565, Japan

Received September 14, 1982

The C=C bond of an olefinic ligand in square-planar, d⁸ metal-olefin complexes has generally been accepted,^{1,2} except for (5-methylenecycloheptene)platinum dichloride,³ to lie perpendicular to the coordination plane. The reason for the perpendicular or "upright" coordination was ascribed² primarily to unfavorable steric interactions with the cis ligands in the parallel or "in-plane" one. Such steric interactions also constitute a major portion of the olefin rotation barrier.² We have recently found that such barriers in [Pt(η^3 -CH₂CMeCH₂)(PPh₃)(olefin)]PF₆ (**1**^{4a} olefin = CH₂=CH₂, **1a**; (*E*)-MeCH=CHMe, **1b**) are remarkably low for a Pt(II)-olefin complex,^{4b} suggesting very small steric requirements around the olefin. In addition to this, ¹H NMR aspects of **1c** (olefin = CH₂=CHPh; see later) greatly different from those of [Pd(η^5 -C₅H₅)(PPh₃)(CH₂=CHPh)]PF₆ (**2**),⁵ of which the crystallographic study had revealed⁶ the upright coordination of styrene, prompted us to undertake X-ray structural studies of the complexes of type **1**. We describe here the molecular structure of **1c**, which shows the first in-plane coordination of simple monoolefins in square-planar complexes.

The crystals of **1c** belong to the monoclinic system, space group P2₁/n with unit cell dimensions $a = 15.560$ (3) Å, $b = 11.342$ (3) Å, $c = 17.594$ (3) Å, and $\beta = 110.91$ (2)°; $d_c = 1.744$ g cm⁻³ for $Z = 4$.⁷ This crystal is isomorphous with that of **2**⁶ although the metal and the ancillary ligand are different in these two. The structure was solved⁸ by the use of that of **2** and refined aniso-

[†] Department of Applied Chemistry.

[‡] Department of Petroleum Chemistry.

(1) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(2) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(3) Wright, L. L.; Wing, R. M.; Rettig, M. F.; Wiger, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 5950. In this case chelate coordination of two C=C bonds in the ligand molecule compelled the exocyclic one to lie parallel to the coordination plane.

(4) (a) Kurosawa, H.; Asada, N. *J. Organomet. Chem.* **1981**, *217*, 259, and unpublished results. (b) $\Delta G^{\ddagger}_{\text{rot}}$ for **1b** at -55 °C (11.0 kcal/mol) may be compared to those^{4c} of PtCl₂(C₄H₉)(acac) (15.8 kcal/mol) and PtCl₂(C₄H₉)(AsEt₃) (≥ 16 kcal/mol). No frozen 100-MHz ¹H NMR spectra were obtained for **1a** down to -90 °C. However, assuming a chemical shift difference of two protons undergoing site-exchange as 0.5 ppm leads us to calculate $\Delta G^{\ddagger}_{\text{rot}}$ for **1a** at -90 °C as 8.8 kcal/mol. Such chemical shift difference of 0.5 ppm may be a minimum estimate for a complex bearing PPh₃, which exerts a large magnetic anisotropy effect to nearby protons.^{4d,5} (c) Ashley-Smith, J.; Douek, Z.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 128; (d) **1972**, 1776.

(5) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996.

(6) Miki, K.; Shiotani, O.; Kai, Y.; Kasai, N.; Kanatani, H.; Kurosawa, H. *Organometallics*, in press. Unit cell dimensions of **2** are $a = 15.571$ (4) Å, $b = 11.187$ (2) Å, $c = 17.596$ (3) Å, and $\beta = 107.71$ (2)°.

(7) A well-shaped crystal with approximate dimensions 0.25 × 0.30 × 0.40 mm was selected for X-ray analysis. Intensity measurements were carried out on a Rigaku automated four-circle diffractometer using graphite monochromatized Mo K α radiation. Reflections with 2θ up to 54.0° were collected by the θ - 2θ scan technique. The 2θ scan rate was 4° min⁻¹ and the scan width $\Delta 2\theta = (2.5 + 0.70 \tan \theta)$ °. The background intensities were measured for 7.5 s at each end of a scan.*

(8) Because of isomorphism of crystals of **1c** with **2**, the structure of **1c** including the PF₆ anion was at first assumed essentially similar to that of **2** except for the methallyl moiety. The atomic coordinates of **2** except for the Cp group were employed for the initial atomic positional parameters of **1c**. By the isotropic refinement, parameters of these atoms were reasonably converged except for the C(1), C(2), and C(3) atoms of styrene ligand. This behavior of three carbon atoms was later confirmed due to the in-plane coordination of the styrene (see text). The locations of these divergent atoms as well as those of the remaining methallyl group were easily found in the subsequent difference Fourier maps.